Synthesis of Arylrhodium(III) Complexes Using Organomercury Compounds. (*o*-Nitrophenyl)rhodium(III) Complexes. Crystal and Molecular Structures of Chlorobis(2-nitrophenyl-C^1,O)(triphenylphosphine)rhodium and Chlorobis(2-nitrophenyl-C^1,O)carbonylrhodium

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Received April 4, 1988

The reaction between $[Hg(2\text{-}C_6H_4NO_2)_2]$ and $[Rh(\mu\text{-}Cl)(CO)_2]_2$ or $RhCl_3{\cdot}3H_2O$ gives $[Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(CO)]$ or $[Rh\{2\text{-}C_6H_4N(O)O\}_2(\mu\text{-}Cl)]_2$, respectively. PPh_3 reacts with the former giving the product of CO insertion, $[Rh\{2\text{-}C_6H_4N(O)O\}\{2\text{-}C(O)C_6H_4N(O)O\}Cl(PPh_3)]$, and with the later leading to the product of bridge splitting, $[Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(PPh_3)]$. The complex $[Rh\{2\text{-}C_6H_4N(O)O\}_2(\mu\text{-}Cl)]_2$ reacts (i) with other neutral monodentate ligands to give complexes of the type $[Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(L)]$ (L = $AsPh_3$, pyridine), (ii) with neutral bidentate ligands giving complexes $[Rh\{2\text{-}C_6H_4N(O)O\}_2(LL)][Rh\{2\text{-}C_6H_4N(O)O\}_2Cl_2]$ (LL = 1,10-phenanthroline, 2,2′-bipyridine), (iii) with Me_4NCl giving $[Me_4N][Rh\{2\text{-}C_6H_4N(O)O\}_2Cl_2]$, and (iv) with NaX giving $[Rh\{2\text{-}C_6H_4N(O)O\}_2(\mu\text{-}X)]_2$ (X = Br, I). The crystal structures of $[Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(PPh_3)]$ (4) and $[Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(CO)]$ (10) have been determined by X-ray analysis. Complex 4 crystallizes in space group $P2_1/a$ with $a = 20.004$ (5) Å, $b = 10.083$ (2) Å, $c = 14.183$ (3) Å, and $\beta = 105.14$ (2)° and complex 10 in space group $P\bar{1}$ with $a = 6.555$ (2) Å, $b = 8.868$ (2) Å, $c = 13.236$ (3) Å, $\alpha = 104.82$ (2)°, $\beta = 104.51$ (2)°, and $\gamma = 83.88$ (2)°. Both compounds are chiral with both pairs of enantiomers being present in the crystals. Complexes 4 and 10 show discrete molecules where the rhodium atoms display distorted octahedral coordination geometries with both phenyl groups mutually cis. This is also the relative position of both oxygen donor atoms and of the other two ligands. In 4, PPh_3 and chloro ligands are trans to a carbon and an oxygen atom, respectively, while in 10, CO and chloro ligands are trans to an oxygen and a carbon atom, respectively. By comparing rhodium–ligand bond lengths in both complexes, the order of the trans influence is shown to be aryl > CO > Cl = PPh_3 > $O(NO)C_6H_4$. The N–O(Rh), C–N, and C–C bond distances in the nitrophenyl groups are compared with data from other 2-nitrophenyl complexes that we have previously characterized.

Introduction

The use of organomercury compounds in the synthesis of organometallics is well-known,[1] but there exist relatively few studies of their specific applications, i.e. syntheses that cannot be achieved with other transmetalating reagents, especially the classical organolithium or Grignard reagents.

However, there are many organomercuric compounds that contain functionalized groups whose lithium or magnesium derivatives are unknown or unstable. The use of these mercurials, as transmetalating reagents in the synthesis of organo derivatives of different elements, should open new areas in organometallic chemistry. With this belief we are developing their use for the synthesis of functionalized aryl complexes of gold,[2-4] palladium,[5,6] platinum,[7] rhodium,[8] tin,[9] and thallium.[10]

One of the aryl groups that we are transferring from mercury to different metallic centers is 2-nitrophenyl.[3-5,7,8] The lithium derivative is thermally very unstable.[11] In fact it has only been used scarcely[12] in spite of the well-

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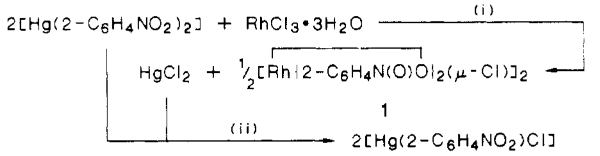
Scheme I. Suggested Reaction Pathway in the Synthesis of 1



documented interest in the synthesis of nitroaryl complexes.[13] In this paper we report the synthesis of (2-nitrophenyl)rhodium(III) complexes.

Two different types of transmetalation reactions are reported in this paper. First, the classical interchange reaction of aryl by chloro ligands from the mercurial to another metallic center (e.g. $R_2Hg + -M-Cl \rightarrow RHgCl + -M-R$). This transmetalation reaction has rarely been studied for the synthesis of rhodium complexes.[15] Second, a redox reaction between $[Hg(2-C_6H_4NO_2)_2]$ and $[Rh(\mu-Cl)(CO)_2]_2$ gives metallic mercury and the Rh(III) product which results from the transfer of both aryl groups from mercury to rhodium, $[Rh\{2-C_6H_4N(O)O\}_2Cl(CO)]$. This type of reaction, which we call a redox transmetalation reaction, is well-known in the chemistry of palladium and platinum,[14] but as far as we know, our report is the first example of it in the chemistry of rhodium.

The synthesis and crystal structure of $[Rh\{2-C_6H_4-N(O)O\}_2Cl(CO)]$ was the subject of a preliminary communication[8] in which we concluded that coordination of the 2-nitrophenyl group as a chelating ligand was responsible for the strong electron delocalization which is shown by the shortening and lengthening of several bond distances in the 2-nitrophenyl group. As there exists some controversy about the electron-withdrawing ability of the nitro group in arenes,[16] we thought it of interest to show how coordination of the nitro group and the nature of the metal and the other ligands present in the complex could influence the π-acceptor ability of the nitro group by comparing C–C, C–N, and N–O bond distances. In this paper we analyze such influence using the structural parameters obtained for the two rhodium complexes reported here along with those of other 2-nitrophenyl complexes.

Results and Discussion

The reaction between $RhCl_3 \cdot 3H_2O$ and the mercurial $[Hg(2-C_6H_4NO_2)_2]$ gives, after stirring the mixture in refluxing ethanol, the complex $[Rh\{2-C_6H_4N(O)O\}_2(\mu-Cl)]_2$ (1) (see Scheme I). The result is the same if the molar ratio between the reagents is 1:1, 1:2, or 1:3. The maximum limit of two for the number of aryl groups that $[Hg(2-C_6H_4NO_2)_2]$ transfers to the rhodium center had previously been observed in its reaction[3] with $[AuCl_4]^-$ where only the diaryl complex $[Au(2-C_6H_4NO_2)_2Cl_2]^-$ could be obtained, even when a strong excess of $[Hg(2-C_6H_4NO_2)_2]$ is used. In fact, we have never obtained a triaryl complex from these transmetalation reactions.

The synthesis of 1 when the molar ratio was 1:1 was not unexpected in view of the fact that diarylation also occurs when $[Hg(2-C_6H_4NO_2)_2]$ reacts 1:1 with $[AuCl_4]^-$,[3] $[PdCl_4]^{2-}$,[5] or $[PtCl_4]^{2-}$.[7] We have suggested[5,7] that this could be interpreted by assuming that both aryl groups transfer in a single step [see (i) in Scheme I]. Therefore, the first product of these transmetalation reactions should be a diaryl complex, even when the molar ratio is 1:1. Only in the reaction with the palladium complex was a mono-2-nitrophenyl complex obtained as the final product, and this was because the first product of the reaction, $[Pd\{2-C_6H_4N(O)O\}_2]$, was able to arylate $HgCl_2$ and $[PdCl_4]^{2-}$ to give, in both cases, $[Pd\{2-C_6H_4N(O)O\}(\mu-Cl)]_2$. Therefore, the synthesis of 1, in any molar ratio, is a consequence of the limited arylating ability of $[Hg(2-C_6H_4NO_2)_2]$ and the non-arylation power of 1 with respect to other intermediates in the reaction.

Assuming that both aryl groups transfer simultaneously, $HgCl_2$ should be the byproduct of the reaction. However, the isolated product was always $[Hg(2-C_6H_4NO_2)Cl]$. This also was observed in the other transmetalation reactions.[3,5,7] A reasonable explanation is that $HgCl_2$ reacts with $[Hg(2-C_6H_4NO_2)_2]$ to give $[Hg(2-C_6H_4NO_2)Cl]$ [see (ii) in Scheme I]. In fact, we have shown in a separate reaction that this occurs.

Complex 1 is only slightly soluble in most organic solvents (e.g. Cl_2CH_2, acetone) except in those with certain donor ability (e.g. EtOH or CH_3CN), probably because of the formation of adducts. However, it is isolated unchanged from these solutions. Our proposed dimeric structure for 1 is based on the following arguments. Assuming the classical octahedral coordination for Rh(III), even if both 2-nitrophenyl ligands were chelating, the chloro bridging is required. The IR spectrum of 1 shows the band corresponding to the mode $\nu_{sym}(NO_2)$ at 1265 cm^{-1} and any other in the region where bands appear due to such vibrational mode for uncoordinated nitroaryls (1330–1350 cm^{-1}). This can be taken as evidence for both 2-nitrophenyl groups being chelating ligands.[3,5,7] Second, the following main peaks were observed in its mass spectrum: m/z (relative intensity) 764 (M, 7.3); 607 (M − $ClC_6H_4NO_2$, 48.2); 382 (M/2, 21.1), and 347 (M/2 − Cl, 100).

The reactions between 1 and NaX in refluxing ethanol (1:2 molar ratio) give the analogous dimeric complexes $[Rh\{2-C_6H_4N(O)O\}_2(\mu-X)]_2$ [X = Br (2), I (3)]. They do not conduct in acetone and show $\nu_{sym}(NO_2)$ at 1260 cm^{-1}.

Addition of PPh_3, $AsPh_3$, or pyridine (py) to suspensions of 1 in Cl_2CH_2 (2:1 molar ratio) gives solutions from which the complexes $[Rh\{2-C_6H_4N(O)O\}_2Cl(L)]$ [L = PPh_3 (4), $AsPh_3$ (5), py (6)] can be isolated. Complex 4 is also obtained even if a molar ratio of 6:1 is used.

The inertness (or the strength) of the Rh–O bond in 1 contrasts with that observed for the Pd–O bond in $[Pd\{2-C_6H_4N(O)O\}(\mu-Cl)]_2$ because it reacts with PPh_3 to give the products of cleaving first the Pd–O bond ([Pd{2-

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$C_6H_4NO_2\}(\mu\text{-Cl})(PPh_3)]_2$) and then the bridge (*trans*-[Pd$\{2\text{-}C_6H_4NO_2\}Cl(PPh_3)_2$]). Other 2-nitrophenyl complexes of Pd and Pt (e.g. [M$\{2\text{-}C_6H_4N(O)O\}_2$]) also show a similar weakness in the O–M bond. According to the results of this and previous studies[5,7,8,17] the order of the strength (or inertness) of the O–M bond in these 2-nitrophenyl complexes is Pt(IV) ≪ Rh(III) ≫ Pd(II) > Pt(II). Due to the great number of our unsuccessful attempts to prepare Au(III) complexes conntaining chelating 2-nitrophenyl ligands, starting from those in which such ligands act as monodentate, Pt(II) ≫ Au(III) could be added.

The structure of complex **4** was carried out (see below). Complexes **5** and **6** are probably isostructural with **4** because their IR spectra are almost identical in those regions where absorptions due to the ligands are not present. The band assignable to $\nu_{sym}(NO_2)$ appears at 1270 (**4**, **5**) and 1268 cm^{-1} (**6**) as expected for chelating 2-nitrophenyl ligands.

The reaction of **1** with neutral bidentate ligands such as 1,10-phenanthroline (phen) or 2,2′-bipyridine (bpy) gives complexes [Rh$\{2\text{-}C_6H_4N(O)O\}_2$(LL)][Rh$\{2\text{-}C_6H_4N(O)O\}_2Cl_2$] [LL = phen (**7**), bpy (**8**)]. The formulation of these complexes is based on their analytical data, on which the stoichiometry "Rh$\{2\text{-}C_6H_4N(O)O\}_2Cl(LL)_{0.5}$" results, and on their molar conductivities in acetone [Λ_M = 95 (**7**), 94 Ω^{-1} cm^2 mol^{-1} (**8**)]. Their IR spectra show the $\nu_{sym}(NO_2)$ at 1260 and 1255 cm^{-1}, respectively, according to the chelating nature of the 2-nitrophenyl groups.

The anionic complex in **7** or **8** can be obtained as the salt [Me$_4$N][Rh$\{2\text{-}C_6H_4N(O)O\}_2Cl_2$] (**9**) by reacting **1** with an excess of [Me$_4$N]Cl. Its IR spectrum shows the $\nu_{sym}(NO_2)$ at 1265 cm^{-1}. However, in solution, some type of association must exist among both ions given that its molar conductivity (Λ_M) is as low as 31 Ω^{-1} cm^2 mol^{-1} in acetone.

The reaction between [Hg(2-$C_6H_4NO_2)_2$] and [Rh(μ-Cl)(CO)$_2$]$_2$ to give Hg and [Rh$\{2\text{-}C_6H_4N(O)O\}_2$Cl(CO)] (**10**) was the subject of a preliminary communication.[8] This reaction gave other products that could not be isolated. However, **10** was the main product of this reaction (50% yield).

In order to prepare a (2-nitrophenyl)rhodium(I) complex we treated [Rh(μ-Cl)(CO)$_2$]$_2$ and [Pd$\{2\text{-}C_6H_4N(O)O\}_2$]. (This complex had been shown to be a good arylating agent.[5]) However, the reaction gave Pd metal and **10** in a better yield than the one using [Hg(2-$C_6H_4NO_2)_2$] (76%); no other secondary product was observed. As far as we know, this is the first reported redox transmetalation reaction of the type Pd(II) + Rh(I) → Pd(0) + Rh(III).

The reaction between **10** and PPh$_3$ gives the complex [Rh$\{2\text{-}C_6H_4N(O)O\}\{2\text{-}C(O)C_6H_4N(O)O\}Cl(PPh_3)$] (**11**) (molar ratio 1:1) that results from the insertion of CO into one of the C–Rh bonds. The same complex is isolated if a 1:3 molar ratio is used. By IR in dichloromethane, the disappearance of the band corresponding to ν(CO) in **10** (at 2096 cm^{-1}) and the observation of a new one at 1650 cm^{-1} (corresponding to the benzoyl group) are almost instantaneous. The molecular weight, measured in chloroform (isopiestic method), confirms the mononuclear nature of **11**.

Crystal Structure of Complexes 4 and 10. The crystal structure of complex **10** was the subject of a preliminary communication.[8] In Table I, some of the more relevant bond distances and angles, for both complexes, are shown.

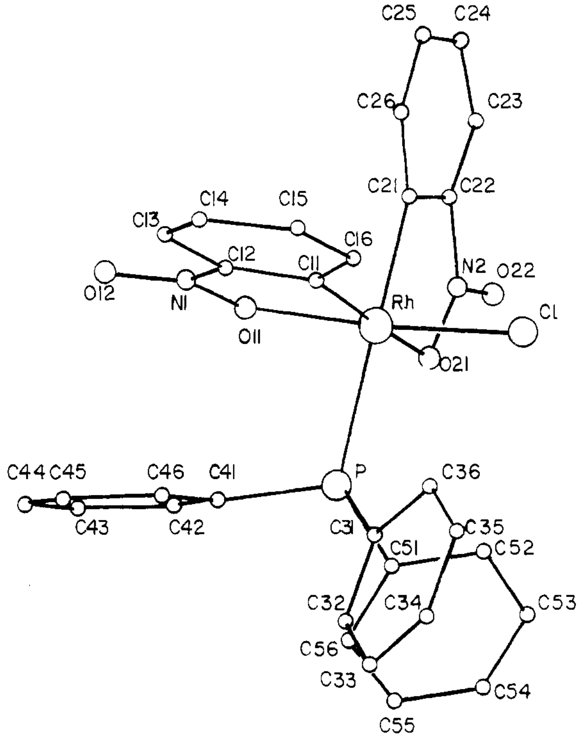

Figure 1. A view of the structure of complex **4**.

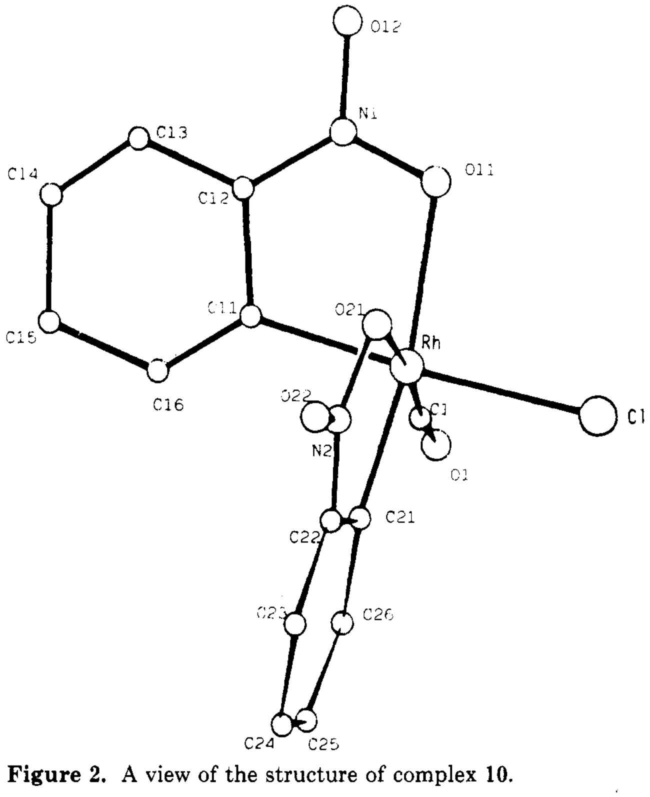

Figure 2. A view of the structure of complex **10**.

The structures of both complexes, **4** and **10**, consist of discrete molecules where the rhodium atoms display a distorted octahedral coordination with both phenyl groups, oxygen donor atoms, and the other two ligands. In complex **4** (see Figure 1), PPh$_3$ and chloro ligands are trans to a carbon and an oxygen atom, respectively, while in complex **10** (see Figure 2), CO and chloro ligands are trans to an oxygen and a carbon atom, respectively. Both complexes are chiral with both pairs of enantiomers being

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Table I. Main Bond Lengths (Å) and Angles (deg) for Complexes 4 and 10

	complex 4		complex 10	
	C(2*x*)[a]	C(1*x*)	C(2*x*)	C(1*x*)
N–O(1)	1.261 (20)	1.329 (18)	1.375 (5)	1.283 (5)
N–O(2)	1.197 (19)	1.232 (22)	1.171 (6)[b]	1.321 (4)
N–C(2)	1.460 (20)	1.414 (26)	1.362 (5)	1.378 (5)
C(1)–C(2)	1.392 (22)	1.383 (28)	1.286 (6)	1.499 (5)
C(2)–C(3)	1.378 (28)	1.405 (26)	1.471 (6)	1.436 (5)
C(3)–C(4)	1.313 (29)	1.307 (34)	1.508 (7)	1.233 (7)
C(4)–C(5)	1.449 (27)	1.441 (37)	1.298 (8)	1.493 (6)
C(5)–C(6)	1.345 (29)	1.380 (29)	1.407 (6)	1.488 (5)
C(6)–C(1)	1.372 (20)	1.384 (26)	1.568 (6)	1.296 (6)
Rh–C(1)[c]	2.041 (16) [P]	1.961 (17) [O]	1.984 (4) [O]	2.041 (3) [Cl]
Rh–O(1)	2.205 (11) [C]	2.032 (12) [Cl]	2.135 (4) [CO]	2.219 (3) [C]
Rh–Cl	2.327 (5) [O]		2.416 (1) [C]	
Rh–P	2.436 (5) [C]			
Rh–C(1)			1.833 (5) [O]	
O(1)–N–O(2)	118.7 (15)	119.9 (13)	111.0 (3)	119.2 (4)
O(1)–N–C(2)	116.6 (15)	119.0 (13)	123.7 (3)	117.5 (3)
O(2)–N–C(2)	124.6 (15)	121.1 (15)	123.3 (3)	123.2 (4)
N–C(2)–C(1)	115.4 (16)	115.8 (15)	116.3 (3)	119.3 (3)
C(2)–C(1)–Rh	113.7 (13)	114.6 (10)	109.7 (3)	115.7 (3)
O(11)–Rh–C(11)	81.4 (6)		81.1 (1)	
O(21)–Rh–C(21)	78.2 (5)		83.2 (2)	
C(11)–Rh–C(21)	95.2 (7)		96.8 (2)	
O(11)–Rh–O(21)	91.7 (4)		79.9 (1)	
Cl–Rh–O(21)	88.1 (3)		87.4 (1)	
Cl–Rh–C(11)	98.3 (6)		174.8 (1)	
Cl–Rh–P	94.8 (2)			
O(11)–Rh–P	89.8 (3)			
Cl–Rh–C(1)			95.3 (1)	
O(11)–Rh–C(1)			105.8 (2)	

[a] The parameters corresponding to the ligands containing the C(1*x*) and C(2*x*) phenyl rings atoms are under the headings C(1*x*) and C(2*x*), respectively. [b] See text. [c] The atom trans is shown in brackets.

Table II. Average Values for N–O(M) [M = Pd(II), Pt(II), and Pt(IV)], N–O, C–N, and C–C Bond Distances in Chelating (R_2) and Monodentated (R_1) 2-Nitrophenyl Ligands[4b,5,7,8,12c,17]

	average values		complex 4		complex 10	
	R_2	R_1	C(1*x*)	C(2*x*)	C(1*x*)	C(2*x*)
N–O(M)[a]	1.269 (12) [5]		1.329 (18)	1.261 (20)	1.283 (5)	1.375 (5)
N–O	1.217 (16) [4]	1.216 (14) [10]	1.232 (22)	1.197 (17)	1.321 (4)	*b*
C–N	1.405 (19) [4]	1.470 (30) [5]	1.414 (26)	1.460 (11)	1.378 (5)	1.362 (5)
C–C	1.391 (10) [13]		*b*		1.233 (7)–1.298 (8) (×4)[c] 1.407 (6)–1.436 (5) (×2) 1.471 (5)–1.568 (6) (×6)	

[a] In brackets is indicated the number of values used to average (only those with standard deviations ≤ 0.009). [b] See text and Table I. [c] The number *N* of C–C bond distances included in the range is denoted by (×*N*).

present in the crystals. By comparing Rh–C, Rh–O, and Rh–Cl bond distances in complexes **4** and **10** (see Table I) the following sequence of trans influence results: aryl > CO > Cl ≈ PPh_3 > $O(ON)C_6H_4$. The position of PPh_3 is the main difference on this scale with respect to that usually reported[18] for four coordinated Pt(II) complexes: aryl ≥ PR_3 > CO ≈ Cl > OR_2.

We shall discuss first the structural data of complex **4** because N–O, C–N, and C–C bond distances are more similar to those in other complexes containing chelating 2-nitrophenyl ligands (which will be designated as R_2 ligands to distinguish them from the monocoordinated ones that we shall represent by R_1), while the presence of CO in complex **10** is reflected throughout the molecule, giving singular values for these parameters.

The only bond lengths of the nitrophenyl groups in complex **4**, significantly different from average values found in R_2 ligands (see Table II), are N–O(M) of the 2-nitrophenyl group which contains the C(11) to C(16) atoms [we shall call it the C(1*x*) ligand] and the C–N of the C(2*x*) ligand. These differences could be due to the different nature of the ligands trans to the oxygen atom and the phenyl group. Because the precision in the data of the C–C bond distances in **4** is low, we cannot compare these values with the average.

To justify the lengthening of the N–O(M) bond distances and the shortening of the C–N bond lengths in R_2-type ligands with respect to the corresponding parameters in R_1-type ligands (see Table II), we have postulated that formation of a $p\pi(O) \rightarrow d\pi(M)$ bond should weaken the N–O bond and should leave the $p_z(N)$ more accessible to a $p_z\pi(C) \rightarrow p_z\pi(N)$ bonding. In addition, the planarity of all the R_2 groups must result in maximum overlap of the two orbitals leading to an even stronger C–N interaction. In low-spin octahedral complexes of d^6 ions, like Rh(III), the π bonding, if it exists, should be of the type $p\pi(O) \rightarrow p\pi(M)$.

However, it seems that, the $p_z\pi(C) \rightarrow p_z\pi(N)$ bonding interaction in 2-nitrophenyl complexes is only observed if the nitro group coordinates. Only the planarity of the ligand is not sufficient for it. Thus, in one of the two different molecules present in the unit cell of [Au(2-$C_6H_4NO_2$)($AsPh_3$)][4b] in which the Au–O distance reveals

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(18) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders Co.: Philadelphia, 1977; p 705.

a weak bonding interaction, the C–N bond length [1.426 (6) Å] is in the range expected for an R_2 group. By the contrary, in *cis*-[Pt(2-$C_6H_4NO_2)_2(PPh_3)_2$][12c] [C–N = 1.482 (9) and 1.474 (9) Å] or in the other molecule in the unit cell of [Au(2-$C_6H_4NO_2$)($AsPh_3$)] [C–N = 1.518 (7) Å] the C–N bond lengths are normal for R_1 nitrophenyl ligand in spite of the planarity of these groups.

However, the C–C bond distances in R_1 and R_2 ligands are not significatively different (see Table II) in spite of the different $P_z\pi(C) \rightarrow P_z\pi(N)$ bonding interaction, with only two exceptions. These are both molecules in the unit cell of [Au(2-$C_6H_4NO_2$)($AsPh_3$)][4b] and complex **10**. The first one shows in the molecules with the biggest Au–O interaction three values longer than the average [range 1.483 (7)–1.491 (7) Å] and in the other one shows two values longer [1.484 (10), 1.477 (7) Å] and one value shorter [1.348 (7) Å] than the average.

However, it is in complex **10** where the $P_z\pi(C) \rightarrow P_z\pi(N)$ bonding interaction is more evident because in each ring there are two very short, one normal, and three long or very long bond distances (see Table II). The different sequence of C–C bond lengths in each ring could be due to the different nature of the ligands trans to the oxygen atom and phenyl ligand.

Given that the main difference between **10** and all the other 2-nitrophenyl complexes is the presence of CO in **10**, its singular structural parameters could be due to the great π-acceptor ability of this ligand. This could enhance the electron-withdrawing capacity of the metal center which via the carbon atom and the nitro group should lead to a net removal of electron density from phenyl rings' HOMO. This could explain why **10** is the complex with the greater number of long C–C bonds and the longest ones. The dual mechanism through which the metal removes electron density could also explain why the sequence of long and short C–C bond distances was not the classical one for a nitroaromatic compound. It is likely that only in complex **10** the $p\pi(O) \rightarrow \pi(M)$ bonding is of relevant importance, while in the other complexes the observed structural changes may be mainly due to inductive effects.

The strong C–N bonding is demonstrated by the very short C–N bond lengths and also by the weakening of the N–O bonds. This last effect is also unique for complex **10**. If the shortening of the N(2)–O(22) bond length [1.171 (6) Å] is not considered [because it is due to disorder of the oxygen atom, as indicated by the thermal parameters], the lengthening of the N–O bond lengths is observed not only in the N–O(Rh) distances [N(1)–O(11) = 1.283 (5) Å; N(2)–O(21) = 1.375 (5) Å] but also, for the first time, in one N–O bond distance [N(1)–O(12) = 1.321 (4) Å].

Some Considerations about the Electron Withdrawing of the Nitro Group in 2-Nitroaryl Complexes. Very recently Politzer[16d] have intervened in the controversy about the electron-withdrawing ability of the nitro group in arenes showing theoretically that a very small degree of conjugation between the nitro group and the aromatic ring exists even when they are coplanar. Our structural data lead to the same conclusion for the R_1 groups whether they are planar or not. However, we can add that if the nitro group is coordinated to a metal, which is also bonded to the ortho carbon atom, (R_2 groups), two different structural situations can be observed. In both cases, a weakening of the N–O(M) bond and a strengthening of the C–N bond occur. The difference rest on the existence or not of any significative changes in C–C bond distances in the ring. In the only case where these C–C changes have been clearly observed, in complex **10**, it seems that the presence on a strong π-acceptor ligand, such as CO, is responsible for the withdrawing of electron density of the nitro group from the aromatic ring. When only the weakening of the N–O(M) bond and the strengthening of the C–N bond is observed, as a consequence of coordination, the structural changes could mainly be due to inductive effects.

Experimental Section

Infrared spectra, the C, H, and N analyses, conductance measurements, melting point and molecular weight determinations, and mass spectra were recorded as described elsewhere.[7] Reactions were stirred at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture unless otherwise stated. Mercury,[19] rhodium(I),[20] and palladium[5] complexes were obtained as reported. All compounds, except **1** were recrystallized by addition of *n*-hexane to their dichloromethane solutions. Yields refer to recrystallized compounds.

Preparation of [Rh{2-C_6H_4N(O)O}$_2$(μ-Cl)]$_2$ (1). To a solution of $RhCl_3 \cdot 3H_2O$ (60 mg, 0.218 mmol) in EtOH (25 cm^3) was added solid [Hg(2-$C_6H_4NO_2)_2$] (203 mg, 0.456 mmol). After being refluxed 1 h, the resulting solution was cooled (0 °C) and the suspension was filtered to remove [Hg(2-$C_6H_4NO_2$)Cl]. To the resulting solution (10 cm^3) was added water to precipitate complex **1** as an orange compound (70 mg, 81% yield; mp 295 °C). It can be recrystallized by the addition of *n*-hexane to a 10/1 dichloromethane/acetonitrile solution of **1**. Anal. Calcd for $C_{24}H_{16}N_4Cl_2O_8Rh_2$: C, 37.68; H, 2.11; N, 7.32. Found: C, 37.22; H, 1.94; N, 7.74.

Preparation of [Rh{2-C_6H_4N(O)O}$_2$(μ-X)]$_2$ [X = Br (2), I (3)]. To a solution of **1** (100 mg, 0.13 mmol) in refluxing EtOH (10 cm^3) was added solid NaX (X = Br, 27 mg, 0.26 mmol; X = I, 40 mg, 0.27 mmol). After $^1/_2$ h the solution was cooled to room temperature and water added (60 cm^3) and left overnight. The resulting suspension was filtered and the solid washed with diethyl ether and air-dried to give **2** (65 mg, 61% yield; decomposes at 305 °C) or **3** (39 mg, 63% yield; decomposes at 277 °C) as red solids. Anal. Calcd for **2**, $C_{24}H_{16}N_4Br_2O_8Rh_2$: C, 35.60; H, 1.90; N, 6.92. Found: C, 35.18; H, 2.06; N, 7.26. Anal. Calcd for **3**, $C_{24}H_{16}N_4I_2O_8Rh_2$: C, 30.41; H, 1.70; N, 5.91. Found: C, 30.63; H, 1.71; N, 5.64.

Preparation of [Rh{2-C_6H_4N(O)O}$_2$Cl(PPh_3)] (4). To a solution of **1** (70 mg, 0.091 mmol) in a mixture of dichloromethane (10 cm^3) and acetonitrile (1 cm^3) was added solid PPh_3. After 1 h the solution was concentrated (till 3 cm^3) and diethyl ether (5 cm^3) and *n*-hexane (20 cm^3) were slowly added. The resulting suspension was filtered and the solid washed with *n*-hexane (2 × 5 cm^3) and air-dried to give **4** as a red solid (108 mg, 92% yield; mp 187 °C dec). Anal. Calcd for **4**, $C_{30}H_{23}N_2ClO_4PRh$: C, 55.88; H, 3.59; N, 4.34. Found: C, 55.58; H, 3.54; N, 4.32. Single crystals of compound **4** were obtained by slow diffusion of *n*-hexane onto a saturated solution of **4** in CH_2Cl_2.

Preparation of [Rh{2-C_6H_4N(O)O}$_2$Cl(L)] [L = $AsPh_3$ (5), py (6)]. To a suspension **1** (50 mg, 0.065 mmol) in dichloromethane (10 cm^3) was added solid $AsPh_3$ (40 mg, 0.13 mmol) or py (0.25 cm^3). After 1 h the solution was concentrated (till 2 cm^3) and *n*-hexane (20 cm^3) was slowly added. The resulting suspension was filtered and the solid washed with *n*-hexane (2 × 5 cm^3) and air-dried to give **5** or **6** as orange (68 mg, 76% yield; mp 183 °C) or red solids (58 mg, 85% yield; mp 178 °C), respectively. Anal. Calcd for **5**, $C_{30}H_{23}N_2AsClO_4Rh$: C, 52.31; H, 3.36; N, 4.07. Found: C, 51.91; H, 3.23; N, 4.01. Anal. Calcd for **6**, $C_{17}H_{13}N_3AsClO_4Rh$: C, 44.23; H, 2.84; N, 9.10. Found: C, 43.48; H, 2.70; N, 8.77.

Preparation of [Rh{2-C_6H_4N(O)O}$_2$(LL)][Rh{2-C_6H_4N(O)O}$_2Cl_2$] [LL = phen (7), bpy (8)]. To a suspension of **1** (50 mg, 0.065 mmol) in dichloromethane (10 cm^3) was added solid 1,10-phenanthroline (23.4 mg, 0.13 mmol) or bpy (20.4 mg, 0.13 mmol). After 1 h the solution was concentrated (till 2 cm^3) and

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Table III. Final Atomic Coordinates (×10⁴) for Non-Hydrogen Atoms and Equivalent Temperature Coefficient[a] of Complex 4

atom	x	y	z	B_{eq}, Å^2
Rh	9331 (1)	1154 (1)	7355 (1)	2.43 (7)
Cl	9432 (2)	−605 (4)	8445 (3)	3.56 (25)
O(11)	9315 (5)	2635 (11)	6377 (8)	3.09 (64)
N(1)	9671 (6)	3697 (16)	6780 (13)	3.17 (101)
O(12)	9672 (5)	4683 (13)	6268 (10)	4.74 (81)
C(11)	9930 (8)	2426 (18)	8231 (14)	2.71 (109)
C(12)	9996 (8)	3626 (20)	7791 (15)	3.49 (118)
C(13)	10407 (10)	4706 (19)	8224 (17)	5.00 (132)
C(14)	10722 (12)	4576 (25)	9151 (21)	6.83 (174)
C(15)	10699 (10)	3361 (24)	9677 (17)	6.31 (144)
C(16)	10309 (10)	2318 (18)	9191 (15)	4.02 (122)
O(21)	8753 (5)	−183 (11)	6195 (8)	3.34 (67)
N(2)	9148 (7)	−868 (14)	5827 (12)	2.95 (95)
O(22)	8910 (6)	−1683 (12)	5219 (10)	4.42 (77)
C(21)	10112 (7)	297 (15)	6886 (12)	2.08 (89)
C(22)	9895 (8)	−659 (15)	6163 (13)	2.32 (102)
C(23)	10304 (11)	−1386 (16)	5707 (14)	3.86 (121)
C(24)	10969 (11)	−1117 (19)	5975 (15)	4.31 (125)
C(25)	11247 (10)	−190 (20)	6760 (15)	4.44 (126)
C(26)	10816 (9)	463 (16)	7184 (14)	3.56 (112)
P	8300 (2)	2078 (4)	7712 (4)	2.42 (29)
C(31)	8238 (7)	2218 (16)	8954 (13)	2.07 (102)
C(32)	7683 (10)	2889 (22)	9145 (21)	6.63 (158)
C(33)	7583 (14)	2987 (30)	10092 (27)	9.46 (209)
C(34)	8077 (16)	2401 (25)	10825 (17)	6.20 (170)
C(35)	8629 (12)	1760 (20)	10674 (23)	5.75 (165)
C(36)	8729 (9)	1694 (16)	9757 (18)	3.68 (117)
C(41)	8162 (7)	3743 (16)	7203 (15)	2.81 (104)
C(42)	7910 (8)	3909 (20)	6220 (17)	3.43 (119)
C(43)	7873 (8)	5189 (23)	5796 (14)	3.30 (112)
C(44)	8098 (9)	6261 (21)	6400 (21)	5.17 (143)
C(45)	8346 (10)	6130 (22)	7366 (18)	5.00 (138)
C(46)	8395 (8)	4851 (20)	7788 (13)	3.36 (111)
C(51)	7519 (8)	1158 (16)	7138 (11)	2.52 (99)
C(52)	7557 (8)	−236 (18)	7196 (12)	2.78 (104)
C(53)	6975 (9)	−1001 (18)	6812 (13)	4.26 (111)
C(54)	6359 (8)	−428 (19)	6357 (13)	3.69 (108)
C(55)	6322 (7)	895 (19)	6297 (13)	3.42 (99)
C(56)	6880 (7)	1709 (15)	6639 (12)	2.77 (92)

[a] B_{eq} is given by the express $8\pi^2/3\sum U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

diethyl ether (15 cm^3) was slowly added. The resulting suspension was filtered and the solid washed with diethyl ether (3 × 5 cm^3) and air-dried to give **7** or **8** as orange (48 mg, 78% yield; mp 186 °C dec) or yellow ochre solids (50 mg, 83% yield; mp 203 °C dec), respectively. Anal. Calcd for **7**, $C_{36}H_{24}N_6Cl_2O_8Rh_2$: C, 45.74; H, 2.56; N, 8.89. Found: C, 46.09; H, 2.98; N, 8.10. Anal. Calcd for **8**, $C_{34}H_{24}N_6Cl_2O_8Rh_2$: C, 44.32; H, 2.62; N, 9.12. Found: C, 44.20; H, 3.17; N, 9.67.

Preparation of $[Me_4N][Rh\{2\text{-}C_6H_4N(O)O\}_2Cl_2]$ (9). To a solution of $[Me_4N]Cl$ (25 mg, 0.228 mmol) in ethanol (5 cm^3) was added solid **1** (50 mg, 0.065 mmol), and the mixture was refluxed during 30 min. The resulting suspension was filtered and the solid washed with diethyl ether (2 × 5 cm^3) and air-dried to give **9** as dark red solid (45 mg, 70% yield; mp 271 °C dec). Anal. Calcd for **9**, $C_{16}H_{20}N_3Cl_2O_4Rh$: C, 39.05; H, 4.10; N, 8.54. Found: C, 39.05; H, 4.02; N, 8.30.

Preparation of $[Rh\{2\text{-}C_6H_4N(O)O\}_2Cl(CO)]$ (10). (a) Using $[Pd\{2\text{-}C_6H_4N(O)O\}_2]$. To a solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (111 mg, 0.225 mmol) in diethyl ether (15 cm^3) was added solid $[Pd\{2\text{-}C_6H_4N(O)O\}_2]$ (200 mg, 0.57 mmol), and the mixture was stirred overnight. The resulting suspension was filtered and the solution concentrated to dryness. The resulting solid was extracted with acetone (10 cm^3), the solution concentrated (till 2 cm^3), and n-hexane (15 cm^3) added. The suspension was filtered and the solid washed with n-hexane (3 × 5 cm^3) and air-dried to give **10** as a yellow solid (140 mg, 76% yield). **(b) Using $[Hg(2\text{-}C_6H_4NO_2)_2]$.** To a solution of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (80 mg, 0.205 mmol) in dichloromethane (20 cm^3) solid $[Hg(2\text{-}C_6H_4NO_2)_2]$ (183 mg, 0.412 mmol). After 4 h the suspension was concentrated to dryness and the solid extracted with diethyl ether (19 cm^3). The resulting solution was concentrated (till 2 cm^3) and n-hexane (15 cm^3) slowly added. The suspension was filtered and the solid air-dried to give **10** as a yellow solid (93 mg, 50% yield; mp 213 °C). Anal. Calcd for **10**, $C_{13}H_8N_2ClO_5Rh$: C, 38.05; H, 1.96; N, 6.82. Found: C, 37.68; H, 1.81; N, 6.66. Single crystals of compound **10** were obtained by slow diffusion of n-hexane onto a saturated solution of **10** in diethyl ether.

Table IV. Final Atomic Coordinates (×10⁴; Rh ×10⁵) for Non-hydrogen Atoms and Equivalent Temperature Coefficient[a] of Complex 10

atom	x	y	z	B_{eq}, Å^2
Rh	76187 (5)	10020 (2)	21087 (2)	2.61 (1)
Cl	5389 (2)	3359 (1)	2158 (1)	4.36 (5)
C(1)	9133 (7)	1423 (4)	1229 (3)	3.6 (2)
O(1)	9915 (5)	1719 (3)	668 (3)	4.8 (2)
C(11)	9348 (6)	−1063 (4)	1928 (3)	3.1 (1)
C(12)	7923 (7)	−2374 (4)	1323 (3)	3.7 (2)
C(13)	8892 (7)	−3920 (5)	1163 (3)	4.2 (2)
C(14)	10757 (9)	−4218 (5)	1560 (4)	5.1 (3)
C(15)	12348 (8)	−3013 (5)	2128 (3)	4.2 (3)
C(16)	11287 (7)	−1434 (4)	2344 (3)	3.9 (3)
O(11)	5106 (7)	−546 (4)	1038 (3)	5.5 (3)
N(1)	5879 (5)	−1954 (3)	869 (2)	3.1 (1)
O(12)	4371 (6)	−2960 (4)	442 (3)	4.7 (1)
C(21)	9503 (7)	2103 (5)	3460 (4)	4.3 (2)
C(22)	9078 (6)	1987 (4)	4334 (3)	3.2 (2)
C(23)	10286 (7)	2744 (5)	5410 (3)	4.5 (2)
C(24)	12225 (9)	3484 (5)	5373 (4)	5.5 (3)
C(25)	12674 (8)	3517 (5)	4478 (4)	4.9 (3)
C(26)	11549 (8)	2844 (5)	3431 (4)	4.4 (2)
O(21)	6185 (6)	540 (4)	3273 (3)	5.0 (2)
N(2)	7378 (7)	1183 (4)	4278 (3)	4.4 (2)
O(22)	6852 (8)	1072 (5)	5037 (4)	7.7 (3)

[a] B_{eq} is given by the express $8\pi^2/3\sum U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Preparation of $[Rh\{2\text{-}C_6H_4N(O)O\}\{2\text{-}C(O)C_6H_4N(O)O\}Cl(PPh_3)]$ (11). To a solution of **10** (30 mg, 0.073 mmol) in acetone (10 cm^3) was added solid PPh_3 (19.2 mg, 0.073 mmol), and the mixture was stirred for 1 h. The resulting solution was concentrated (till 2 cm^3) and diethyl ether (15 cm^3) slowly added. The suspension was filtered and the solid washed with diethyl ether (3 × 5 cm^3) and air-dried to give **11** as a pale yellow compound (45 mg, 91% yield; mp 124 °C). Anal. Calcd for **11**, $C_{31}H_{23}N_2ClO_5PRh$: C, 55.34; H, 3.44; N, 4.16. Found: C, 55.09; H, 3.75; N, 4.15. Molecular weight in chloroform (18.4 mg/g of $CHCl_3$): calcd, 673; found, 632.

Crystal Structure Determinations. Complex 4. Crystal data: $C_{30}H_{23}N_2ClO_4PRh$; fw 542; monoclinic, space group $P2_1/a$; a = 20.004 (5) Å, b = 10.083 (2) Å, c = 14.183 (3) Å, β = 105.14 (2)°; V = 2761 (2) Å^3; D_{calcd} = 1.303 g cm^{-3}, Z = 4; $F(000)$ = 1124; λ(Mo K$_\alpha$) = 0.71069 Å; μ(Mo K$_\alpha$) = 2.39 cm^{-1}; 288 K. A prismatic crystal (0.1 × 0.1 × 0.12 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12°$) and refined by least squares. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the ω-scan technique, with a scan width of 1° and a scan speed of 0.03° s^{-1}. A total of 1431 independent reflections were measured every 2 h as orientation and intensity control, and significant intensity decay was not observed. Lorentz–polarization but no absorption corrections were made. The Rh atom was located from a Patterson synthesis, and the remaining non-hydrogen atoms from the DIRDIF computer system.[21] The structure was isotropically and anisotropically refined by full-matrix least-squares method, using the SHELX 76 program.[22] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2|F_o| + 0.0057|F_o|^2$, f, f' and f'' were taken

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(22) Sheldrick, G. M. SHELX, a computer program for crystal structure determination; University of Cambridge: Cambridge, England, 1976.

from ref 23. Hydrogen positions were computed and refined by using a riding model with C–H distances constrained with an overall isotropic temperature factor and anisotropically the remaining atoms. The final R was 0.053 (R_w = 0.054) for all observed reflections. **Complex 10.** Crystal data: $C_{13}H_8N_2ClO_5Rh$, fw 410.58; triclinic; space group $P\bar{1}$; a = 6.555 (2) Å, b = 8.868 (2) Å, c = 13.236 (3) Å, α = 104.82 (2)°, β = 104.51 (2)°, γ = 83.88 (2)°; V = 719.3 (5) Å^3; D_{calcd} 1.89 g cm^{-3}, Z = 2; $F(000)$ = 404; γ(Mo Kα) = 0.71069 Å; μ(Mo K$_\alpha$) = 13.63 cm^{-1}; room temperature; crystal dimensions 0.1 × 0.1 × 0.15 mm; Enraf-Nonius CAD-4 diffractometer; monocromatized Mo K$_\alpha$ radiation; θ–2θ technique; 2664 reflections in the range $2 \leq \theta \leq 25°$, 2140 observed [$I \geq 2.5\sigma(I)$]. Lorentz–polarization and absorption corrections were applied. The structure was solved by direct methods (MULTAN[24]). The structure was refined by treating nonhydrogen atoms anisotropically by full-matrix least-squares methods, using SHELX 76,[22] to a final R value of 0.037 (R_w = 0.036). The function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma^2|F_o| + 0.0037|F_o|^2)^{-1}$ and f, f', and f'' values were taken from ref 23. Hydrogen atoms were not located.

Tables III and IV give the atomic coordinates for non-hydrogen atoms of complexes 4 and 10, respectively.

Acknowledgment. J.V. thanks the Comision Asesora de Investigacion Cientifica y Tecnica (PB85-0295) (Spain) for financial support. The crystallographic work was partially sponsored by a grant of the University of Barcelona (Spain). J.M. is grateful for a grant from ENPETROL S.A., Cartagena, Murcia, Spain.

Registry No. 1, 118041-62-6; 2, 118018-68-1; 3, 118018-69-2; 4, 118018-70-5; 5, 118018-71-6; 6, 118018-72-7; 7, 118018-75-0; 8, 118018-77-2; 9, 118018-78-3; 10, 99491-90-4; 11, 118018-79-4; [Hg(2-$C_6H_4NO_2$)$_2$], 26953-08-2; [Pd{2-$C_6H_4NO_2$}$_2$], 118018-80-7; [Rh(μ-Cl)(CO)$_2$]$_2$, 14523-22-9.

Supplementary Material Available: Tables of anisotropic thermal coefficients of compounds 4 and 10 and computed H atoms of compound 4 (3 pages); listings of observed and calculated structure factors for compounds 4 and 10 (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Molecular Structure of EtGe(SePh)$_3$: An Unusual Example of Alkylation by LiEt$_3$BH

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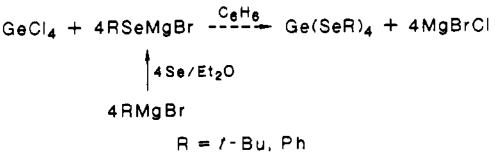
Received April 19, 1988

The reaction of $GeCl_4$ with 4 equiv of Li{SePh}, generated by the reductive cleavage of Ph_2Se_2 with LiEt$_3$BH in tetrahydrofuran, gave a mixture of Ge(SePh)$_4$ and EtGe(SePh)$_3$. These products were separated by fractional crystallization from a hexane solution and characterized by ^{1}H and ^{77}Se NMR spectroscopy and single-crystal X-ray diffraction. The latter compound is the first well-characterized example of ethylation of a metal halide via LiEt$_3$BH. Crystals of Ge(SePh)$_4$ are orthorhombic, $Pbca$, with a = 17.111 (2) Å, b = 8.513 (1) Å, c = 8.455 (3) Å, and Z = 2. The structure was solved by direct methods and refined by the full-matrix least-squares method to R = 0.023. Crystals of EtGe(SePh)$_3$ are triclinic, $P\bar{1}$, with a = 10.631 (1) Å, b = 11.022 (2) Å, c = 10.166 (1) Å, α = 115.048 (9)°, β = 99.908 (8)°, γ = 90.864 (9)°, and Z = 2. The structure was solved by the heavy-atom method and refined to R = 0.025. The geometry about the Ge in both compounds is approximately tetrahedral. The Ge–Se bond distances are in the range 2.344–2.356 Å, and the Ge–C distance in EtGe(SePh)$_3$ is 1.952 Å.

Introduction

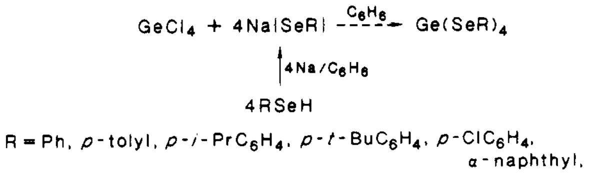
Although selenium ligand chemistry involving transition metals has been the subject of considerable work,[1] relatively little has been reported concerning analogous materials with main group elements such as germanium.[2] An early paper[3] described the synthesis of several derivatives of the type Ge(SeR)$_4$, their characterization being limited to elemental analyses and melting points:



$$\mathrm{GeCl_4 + 4RSeMgBr \xrightarrow{C_6H_6} Ge(SeR)_4 + 4MgBrCl} \qquad (1)$$

$$\mathrm{4RMgBr \xrightarrow{4Se/Et_2O} 4RSeMgBr}$$

R = *t*-Bu, Ph



$$\mathrm{GeCl_4 + 4Na\{SeR\} \xrightarrow{C_6H_6} Ge(SeR)_4} \qquad (2)$$

$$\mathrm{4RSeH \xrightarrow{4Na/C_6H_6} 4Na\{SeR\}}$$

R = Ph, *p*-tolyl, *p*-*i*-PrC$_6$H$_4$, *p*-*t*-BuC$_6$H$_4$, *p*-ClC$_6$H$_4$, α-naphthyl, C$_6$H$_{11}$

Subsequently several other organogermanium compounds incorporating Ge–Se bonds were described ({Me$_2$GeSe}$_3$,[4] Se(GeR$_3$)$_2$ (R = Me,[5] Et,[6] Ph,[7] C$_6$F$_5$[8]), Et$_3$GeSeH,[6b] Et$_3$GeSeSnEt$_3$,[6b] Ph$_3$GeSeSeGePh$_3$,[9] R$_3$GeSeHgGeR$_3$ (R = Et, *i*-Pr),[10] and (*t*-Bu)$_2$Ge(μ-Se)$_2$Ge(*t*-Bu)$_2$)[11]). In addition, crystal structures have been reported for the cyclic polygermanes {(Ph$_2$Ge)$_4$Se}[12] and {(Ph$_2$Ge)$_3$Se$_2$},[13] 1,3-diselena-2,2-dichlorogermyl-[3]-ferrocenophane (Fe(C$_5$H$_4$Se)$_2$GeCl$_2$),[14] and GeSe$_2$[15] as well

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